CHEMICAL STRUCTURE OF A SPORINITE FROM A LIGNITE: COMPARISON WITH A SYNTHETIC SPORINITE TRANSFORMED FROM SPOROPOLLENIN

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INTRODUCTION

The maceral sporinite is thought to be derived from spores and pollen. Both sporinite and sporopollenin, the insoluble cell wall residue after chemical treatment, are considered to have a highly polymerized, cross-linked aliphatic structure with some aromatics (1-3). Many investigators have endeavored to characterize the physical and chemical nature of sporinites (4-7) and sporopollenin (8-11); however, their chemical structures have not been well defined. Furthermore, little is known about how sporopollenin transforms to sporinites during the early stage of coalification.

The aim of the present study is to compare chemical structures of an immature sporinite and its precursor, sporopollenin. In a parallel experiment, the transformation of sporopollenin into a synthetic sporinite has been carried out in the laboratory using thermal catalytic reactions under conditions of simulated catagenetic maturation.

EXPERIMENTAL

Samples

Sporinite. A sporinite material separated from a North Dakota lignite (82% sporinite by petrographic analysis) was treated with 5% HCl, and then refluxed with benzene-methanol (3:1) for 24 hrs. Total extractable material was about 10 wt% of the sample. Analysis of the extracted sporinite yields the following composition: $C_{100}H_{130}N_{0.5}O_{21}$.

Sporopollenin. Sporopollenin was isolated from *Lycopodium clavatum* spores which were refluxed with $CHCl_3$ (24 hr), and then with benzene-methanol 3:1, 24 hr). The yields of total extract and insoluble residue were 55.4 and 44.0 wt%, respectively. The organic solvent extracted residue was then hydrolyzed by refluxing with 6% KOH methanol-water (7:3) solution for 20 hrs. After removal of hydrolyzates, the residue (25 wt% from the original spore) was further treated with 72% H_2SO_4 at 0°-4°C for 12 hrs, and then was refluxed with 3% H_2SO_4 for 10 hrs, filtered, washed with water and methanol, and dried. The yield of sporopollenin, ($C_{100}H_{138}N_{0.6}O_{29}$) was 15.8 wt% from the original spore.

Synthetic Sporinite. Sporopollenin (0.5 g) and 4 g of freshly acid activated montmorillonite clay were ground together and were then placed in a 25 x 2 cm i.d. tube. After evacuation, the sealed tube was inserted to a depth of about 5 cm in a tubular furnace and was heated at 150°C for 2 months.

After the reaction, the mixture was extracted with refluxing benzene-methanol (3:1), chloroform, and finally with ether. To remove the clay, the solvent insoluble residue was treated three times with HCl-HF (1:1) by stirring at room temperature for 24 hours. The yield of synthetic sporinite was 81 wt% with a composition of $C_{100}H_{124}N_{0.1}O_{21}$.

Pyrolysis

A sample (~200 mg) was placed in a 20 x 1 cm i.d. quartz tube; after evacuation the sealed tube was inserted to a depth of about 5 cm in a preheated furnace at 600°C and was heated for 1 minute. The pyrolyzate was extracted with refluxing benzene-methanol (3:1); the yield was generally 38-55 wt%.

Oxidation

In general, a sample (0.3 g) was oxidized with a two-step, buffer-controlled permanganate oxidation (for procedure see ref. 12-13). Before the oxidation, in order to protect phenolic rings from destruction, the sample was methylated with dimethylsulfate -d_6. In general, the yields of oxidation products were about 58-79 wt% for all three samples.

Characterization and Identification Procedures

All mass spectra (GCMS, solid probe) were obtained on a KRATOS MS25/DS55 Data System. Solid probe data were obtained in a precise mass measurement mode. GC separations were made using a 60 m x 0.25 mm bonded OV-1701 fused silica column temperature programmed 50-280°C at 8°/min. Solids were evaporated and pyrolyzed in the source using a direct heating platinum filament probe designed in this laboratory.

Solid ^{13}C spectra were recorded at 2.3 T (25.18 MHz for ^{13}C) on a Bruker Instruments spectrometer, Model CXP-100, in the pulse Fourier transform mode with quadrature phase detection. The ceramic sample spinners had an internal volume of 300 µL and were spun at approximately 4 kHz. Operating parameters in cross-polarization experiments included a spectral width of 10 kHz, a 90° proton pulse width of 4.2 µs (60 kHz proton decoupling field), an acquisition time of 20 ms, a pulse repetition time of 1 s and a total accumulation of 1000 transients. In a typical experiment, 200 W of memory was allocated for data acquisition and was then increased to 4K (2K real data) by zero filling. Before Fourier transformation of the data, the interferogram was multiplied by a decreasing trapezoidal window function after the first 20 data points.

Infrared spectra were obtained by the KBr disk method using an IBM-098/4A FTIR spectrometer.

RESULTS AND DISCUSSION

FTIR and NMR

Solid ^{13}C-CP/MAS and FTIR studies indicate that sporopollenin, synthetic sporinite and sporinite are highly aliphatic. Both natural and synthetic sporinite samples showed very similar FTIR spectra: the absorption band near 1710 cm^{-1} is due to C=O stretching of carbonyl and carboxyl groups. The weak band at around 1615 cm^{-1} may be due to the presence of aromatic rings.

The ^{13}C-CP/MAS spectra of raw spores, isolated sporopollenin, synthetic sporinite and North Dakota sporinite are shown in Figure 1. The spectrum (a) of raw spores indicates the wide variety of carbon structural types which are present. The most prominent feature is the broad absorption found in the aliphatic region, ~15-50 ppm. Sharp resonances appearing at 75 ppm and 105 ppm are typical of polysaccharide structures. In addition, there are two other resonances of lower intensity found in the aliphatic C-O region, ~50-70 ppm. The low-field region consists of several unsaturated carbon resonances (110-150 ppm)

and a reasonably broad absorption centered at 175 ppm which is typical of aliphatic ester groups.

Solvent extraction of the raw spores followed by base (KOH) treatment produces an insoluble material whose solid ^{13}C spectrum (not shown) is devoid of resonances in the low-field region. Further characterization of the solubilized materials by solution ^{13}C-NMR and MS indicates that they are largely lipid structures comprised of unsaturated fatty acids. Subsequent treatment of the insoluble material with H_2SO_4 produces a solid residue which we term sporopollenin. Its ^{13}C spectrum (b) shows the additional diminution in the sharp resonances at 75 and 105 ppm, previously assigned to carbohydrate carbons. What apparently remains is a highly aliphatic polymer containing a relatively high proportion of aliphatic C-O functionalities (presumably aliphatic ether or aliphatic hydroxyl groups), and a small amount of unsaturation. These unsaturated structures are presumed to be olefins which had been formed via dehydration of -OH groups during H_2SO_4 treatment.

Sporopollenin can be readily transformed in the presence of clays at 150°C into an insoluble material whose solid ^{13}C spectrum (c) closely resembles the spectrum (d) obtained for a natural (North Dakota lignite) sporinite sample. There has been a significant reduction in the number of aliphatic C-O groups with the concomitant appearance of new resonances in the unsaturated carbon region (110-155 ppm). At present, we are not certain whether these new resonances are aromatic or olefinic in nature. The fraction of unsaturated carbon (f_u) determined for spectrum (c) and (d) is also comparable: f_u=0.21 for natural sporinite and f_u=0.23 for synthetic sporinite.

Oxidation

As shown in Figure 2, a two-step, buffer-controlled, $KMnO_4$ oxidation of both natural and synthetic sporinites gave qualitatively and quantitatively similar products. Major products were unbranched dicarboxylic acids, while branched dicarboxylic acids and tricarboxylic acids were also identified, but in much lower concentrations. Aliphatic monocarboxylic acids were not detected, contrary to previous reports on several other sporinites (4) and kerogens (14-15). This would seem to imply that our sporinite samples do not have peripheral long-chain alkyl groups. However, sporopollenin yielded only minor amounts of two monocarboxylic acids, C_{16} and C_{18}. The aromatic acids, benzene- and phenol-carboxylic acids were present in low amounts in all three samples.

It is interesting to note that after methylation with dimethylsulphate-$\underline{d}_6$, the oxidation of all three samples produced a mixture of methoxy-$\underline{d}_3$ and regular methoxy benzenecarboxylic acids. This indicates that sporopollenin and sporinite samples contain both hydroxy and methoxy benzene derivatives as structural units. The GCMS analyses of the oxidation products from all samples showed methoxy-$\underline{d}_3$ derivatives are always predominant: OCD_3/OCH_3 ratios for sporinite ~9.4, synthetic sporinite ~8.6 and sporopollenin ~2.9.

While the yields of unbranched dicarboxylic acids for sporinite and synthetic sporinite were much higher than those of branched dicarboxylic acids (see Figure 2), sporopollenin produced relatively large amounts of branched dicarboxylic acids together with some keto-dicarboxylic acids. Most of these branched acids were mono- or di-methyl derivatives, but isoprenoid acids were not detected in any of the samples.

The oxidation of synthetic sporinite produced higher yields of aromatic acids, in particular benzenepolycarboxylic acids (tri-, tetra-, and penta-),

compared with that of sporopollenin. It is obvious that the thermal catalytic reaction promoted alteration of the sporopollenin structure by dehydration, condensation, aromatization, etc. The ratio of aliphatics/aromatics in the oxidation products became close to that of natural sporinite. These trends are typically observed for the transformation of plant biopolymers to geopolymers, such as coals and coal macerals.

Pyrolysis

As expected, the major products obtained from the pyrolysis of both natural and synthetic sporinites (see Figure 3) were long chain alkanes and alkenes. Benzenes, naphthalenes, indanes/tetralins and phenols were minor components. On the other hand, pyrolyzates from sporopollenin were quite different. The most abundant products obtained were naphthalenes, while other aromatics were also found in significant amounts. However, the oxidation, NMR and FTIR studies clearly showed that the sporopollenin has a highly aliphatic structure.

Achari et al. (8) have reported that the pyrolyses of several sporopollenins show the presence of typical carotenoid degradation compounds, including ionene and various naphthalenes in the products. In contrast with the observation by Achari et al., (8) Schenck and co-workers (10) have found benzene and phenol derivatives from the pyrolysis of Lycopodium sporopollenin. However, there was very little evidence for the presence of naphthalenes.

Although we have consistently failed to detect ionene, which is the most important degradation product from β-carotene, significant amounts of various napthalenes have been identified. We do not know, at present, why our results differ from those obtained in two other laboratories. Perhaps, one reason for this discrepancy is that our sporopollenin sample was obtained using a milder isolation procedure ($KOH-H_2SO_4$) than the procedure ($KOH-H_3PO_4$) employed by others (2,10). In any case, sporopollenin, which is a highly aliphatic polymer, produces considerably more aromatics than aliphatics under pyrolysis. It is known that the pyrolysis of polyenes, including non-conjugated polyenes, produces aromatic and cyclic hydrocarbons (8,16-17). Hence, the aliphatic substructures of sporopollenin may well have a substantial number of olefinic double bonds and/or alcoholic OH groups. During pyrolysis, such alcoholic OH groups could easily dehydrate to form polyenes which rapidly aromatize prior to their thermal fragmentation.

SUMMARY

Thermal reactions of sporopollenin with clay minerals produced a geopolymer-like material which closely resembles an immature sporinite in composition, pyrolysis and oxidation products, and spectroscopic properties. Both natural and synthetic (transformed sporopollenin) sporinites have highly polymerized, cross-linked aliphatic structures containing some benzene and phenol ring systems. Several organic oxygen groups also have been identified in these polymeric materials; they are alcoholic and phenolic OH, methoxyl, carbonyl/carboxyl and ether. Among these, alcoholic OH groups appears to be predominant.

Sporopollenin is presumably transformed into immature sporinite by chemical reactions such as dehydration, hydrogen disproportionation, aromatization, etc. Indeed, it is known that these reactions occur during natural evolution (18). For example, conversion of alcohols to olefins and to alkanes, or of cycloalkenes to cycloalkanes and to aromatic hydrocarbons, is known. Polymerization or condensation of olefins involves the formation of aromatic rings. Many of these reactions are promoted by acidic catalysts such as natural clay minerals.

The present study gives some insight into the chemical structures of an immature sporinite and its precursor, sporopollenin, and the chemical transformations leading to sporinite during the early stage of coalification.

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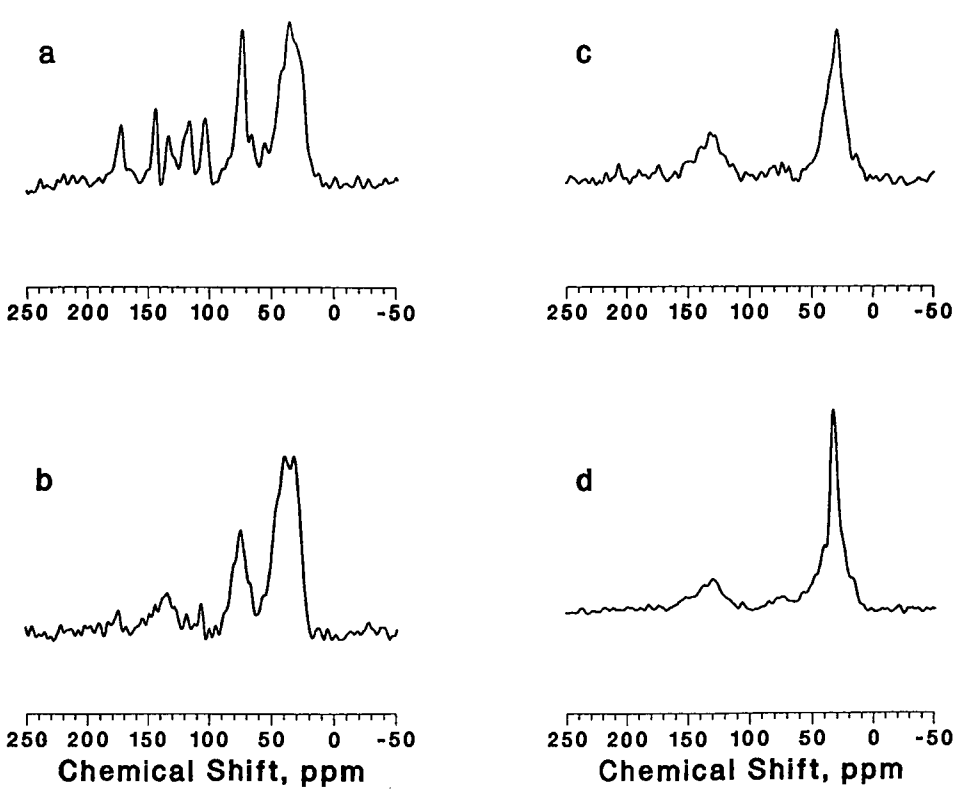

Figure 1. Solid ^{13}C-NMR spectra of (a) raw spores, (b) sporopollenin, (c) synthetic sporinite and (d) North Dakota sporinite.

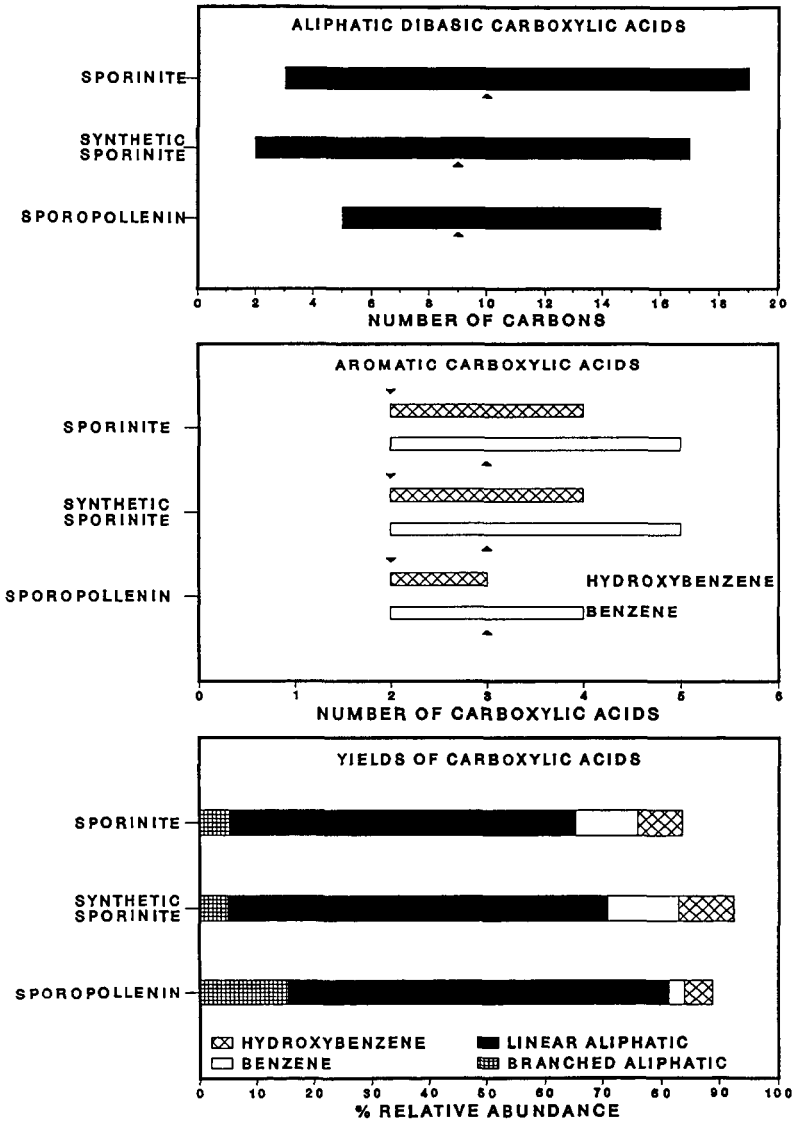

Figure 2. Relative abundances of $KMnO_4$ oxidation products: symbol (▲) indicates most abundant product.

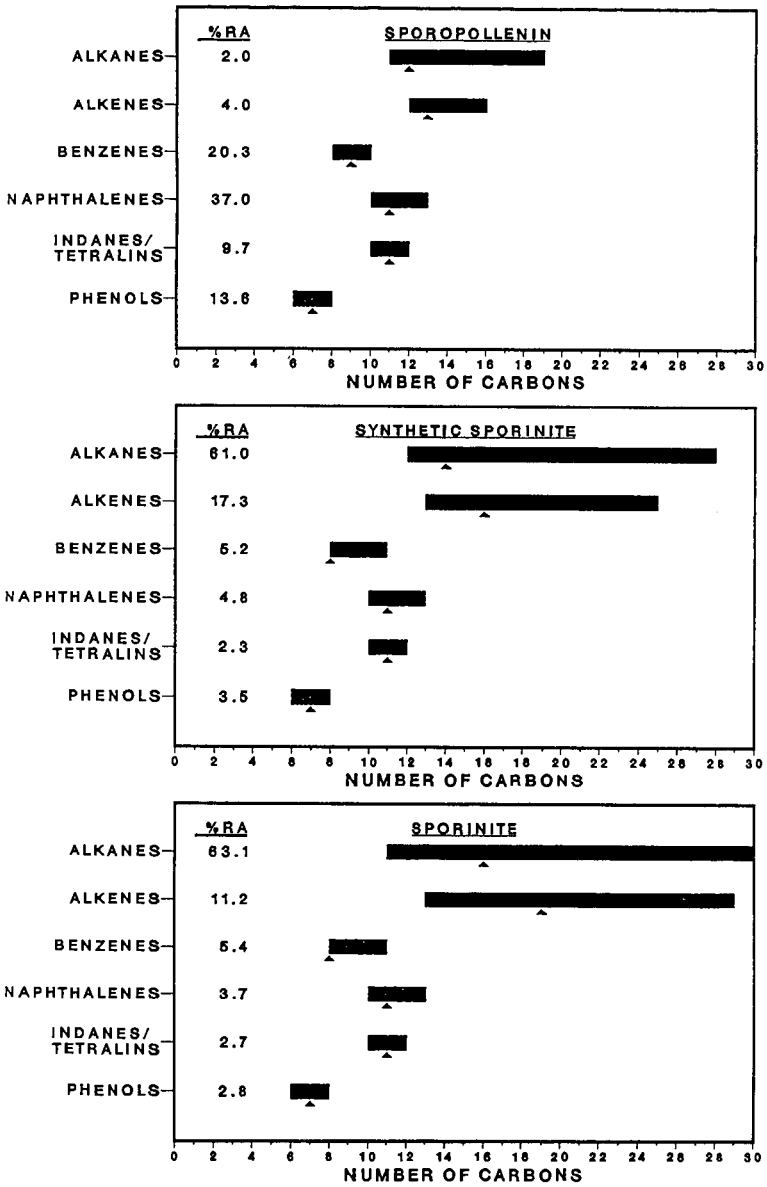

Figure 3. Relative abundances of pyrolyzates: symbol (▲) indicates most abundant product.